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Influence of annealing porous templates in an ammonia atmosphere on gallium nitride growth behaviors in hydride vapor phase epitaxy

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ABSTRACT

Porous templates were fabricated by hydrogen-etching metal organic chemical vapor deposited gallium nitride (GaN); these templates were used as substrates for the growth of GaN via hydride vapor phase epitaxy. The influence of annealing porous templates on GaN growth behavior was investigated. GaN epitaxied on the unannealing porous template followed the Volmer–Weber mode with the void preserved at the growth plane, whereas the GaN film on the annealed porous templates exhibited a layer-by-layer growth and filled the porous material. The GaN crystal quality was characterized by high-resolution XRD and CL, the results indicated that GaN grown with pores preserved at the template interface had a lower dislocation density than that grown with pores filled, and the best GaN film had a TD density of 10^4 cm^{-2}.

1. Introduction

Gallium nitride (GaN) has been proven to have a high performance in high-speed electronics and optical emitters, i.e., laser diodes, light-emitting diodes, and detectors [1]. Given the absence of high-quality epitaxial substrates, efforts have been focused to develop methods that can reduce the dislocation density in heteroepitaxial GaN films. Porous templates, which have been used as substrates, were reported to reduce the dislocation density in GaN films [2–7]. During the epitaxital growth, if the pores had sealed at the interfacial templates, that could reduce the residual stress and prevent the dislocation in the template from penetrating into the epitaxial layer [8]. While the pores at the interface were filled during the growth, the GaN epitaxial layer would replicate the underlying dislocation structure, so the slight reduction of the dislocation densities exist in the overgrown layers as compared with the seed layer [2]. Porous templates can be prepared via anodic etching, reactive ion etching, inductively coupled plasma etching, and hydrogen etching; amongst those methods, the hydrogen etching technique was a convenient method to fabricate porous templates for the growth of GaN at the in situ hydride vapor phase epitaxy (HVPE) reactor [9]. However, to obtain a high-quality GaN epitaxial layer on the H_2-etched GaN/sapphire template, investigating the factors affecting the filling of the pores and its interference with the later epitaxial growth is necessary.

In this paper, porous GaN templates were etched by H_2 at the HVPE growth system, and the HVPE GaN layers were then fabricated on as-etched templates. The influence of annealing porous templates on GaN growth behavior was also investigated.

2. Experiment

The 5-μm-thick GaN on sapphire templates were placed in the HVPE reactor for in situ H_2 etching. To avoid GaN

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decomposition, NH_3 was also introduced into the reactor during heating untill a substrate temperature of 1050 °C, and then, the protective atmosphere was emptied before a mixture of H_2 and N_2 was introduced with the flow rates of 100 sccm and 200 sccm, respectively. Etching was carried out at an H_2 partial pressure of 0.3 atm for 30 min. HVPE growth was immediately performed after the etching process. For comparison, the as-etched GaN, which was annealed in an NH_3 at partial pressure of 0.9 atm for 30 min, was also used to investigate the factors affecting the pores filling and the later epitaxial growth. The total pressure is 0.9 atm in the reactor during etching, annealing, and growth.

The HVPE system used in this study was a home-built horizontal reactor with a rotating quartz susceptor designed for substrates with a diameter of 2 in. GaCl was formed by the reaction between HCl gas and Ga metal, a GaCl synthesis temperature of 800 °C, and an HCl flow of 20 mL/min, which was diluted in 500 mL/min of N_2. HVPE growth was performed at a temperature of approximately 1050 °C, NH_3 flow of 2000 mL/min, and N_2 and H_2 mixture with the flow rates of 500 sccm and 1500 sccm, respectively, as carrier gases. The morphologies of the etched templates and the HVPE-GaN films were observed using a scanning electron microscope (SEM). XRD was carried out to characterize the crystalline qualities of the HVPE-GaN films by using GaN symmetrical (002) and asymmetrical (102) reflections. CL investigation was used to further confirm the dislocation density.

3. Results and discussion

Fig. 1 shows the SEM images of the morphology of the GaN template surface structure and the cross-section structure after H_2 etching. Fig. 1(a and b) corresponds to the porous templates without and after annealing, respectively. The morphology of the H_2-etched template was characterized by the appearance of hillocks and pinholes. These hillocks had an average lateral diameter of 2–8 μm and a typical height difference of hillocks from 1 μm to 3 μm. The diameters of the pinholes were about 100–500 nm with depths of 1–6 μm. Particular weak areas, such as dislocation sites, tend to form pinholes because of the fast vertical etch rate, whereas surfaces with fewer defects are inclined to form a hillock morphology [10]. Fig. 1(b) shows the morphology of the as-etched GaN template that was annealed in an NH_3 atmosphere. A significant surface smoothing and the height difference of hillocks decreasing indicated that the decomposition and regrowth occurred simultaneously on as-etched GaN surface during annealing, the reason for the relatively flat template surface was presumed to be caused by the H-containing species from the decomposition of the NH_3 gas. The species may have attacked the energetically unstable island structures on the GaN surface. Meanwhile, recrystallization occurred on the energetically stable facets during annealing.

Fig. 2 shows the SEM image of the surface morphology on the as-etched GaN templates in which HVPE growth was performed for 30 min. Two distinct types of film morphology were observed, which correspond to the presence or absence of annealing. Fig. 2(a) exhibits a typical SEM image of GaN islands on the unannealed porous template. The specific morphology of the islands is an irregular hexagonal bevel with sidewalls of $(1-101)$ facets. The size of the large islands uniformly ranged between 2.5×10^3 and 4×10^4 μm^2, and the small islands with sizes between 0.5 and 50 μm^2 were observed in the regions between the large islands. Fig. 2(b) shows a representative SEM image of a GaN epitaxial layer grown on the annealed templates. The image shows the smooth surface of GaN with pits, which have diameters of 2–20 μm.

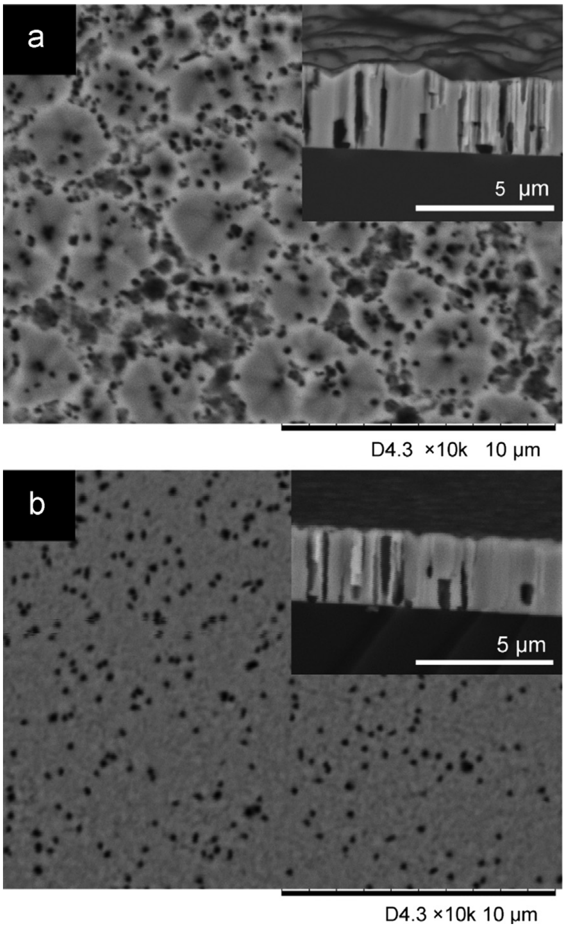

Fig. 1. SEM images of the morphology on the GaN templates after hydrogen etching (a) without annealing and (b) after annealing.

As shown in Fig. 2(a), the GaN growth follows the Volmer–Weber mode with the GaN islands randomly nucleating and growing on the template surface, that is, the deposited N and Ga atoms were more strongly bonded to each other than to the template surface, it indicated that the H_2-etched template interface prevented GaN nucleation or growth. During the H_2-etching process, the GaN decomposition rate can exceed the Ga desorption rate; thus, Ga droplets or a Ga-rich layer was formed on the GaN surface [11]. The Ga droplets catalyze GaN decomposition; accordingly, the Ga droplets hinder epitaxial growth during the HVPE process until they are fully nitridized [12]. On the condition that the H_2-etched template was annealed in an NH_3 atmosphere, the surface of the GaN